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QUANTUM LIMIT STUDIES IN SINGLE CRYSTAL AND PYROLYTIC GRAPHITE

by J. A. Woollam, D. J. Sellmyer, R. O. Dillon and I. L. Spain
Lewis Research Center
Cleveland, Ohio

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Quantum Limit Studies in Single Crystal and Pyrolytic Graphite

John A. Woollam
NASA Lewis Research Center
Cleveland, Ohio 44135

David J. Sellmyer[+*]
Materials Science Center
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

and

Rodney O. Dillon[++] and Ian L. Spain[++]
Department of Chemical Engineering
University of Maryland
College Park, Maryland 20740

I. INTRODUCTION

The occupied regions of momentum space in graphite are confined to very elongated volumes near the hexagonal Brillouin zone edges. The elongation is along the hexagonal axis (c-axis), so that cross-sectional areas perpendicular to that axis are very small. Hence, when magnetic fields are applied parallel to the c-axis, only the n = 0 Landau levels remain below the Fermi energy for fields above 7 tesla.

The energy bands in graphite can be described by a set of seven parameters[2] (including the Fermi energy as a parameter). In a quantizing magnetic field the Landau levels are described by a secular equation determined by diagonalizing the Hamiltonian.[3] A major unusual feature for the levels along the Brillouin zone edge is that the n = 0 Landau level for electrons is independent of magnetic

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[+]Now at Department of Physics, University of Nebraska, Lincoln, Nebraska.

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field, while that for holes is field dependent.

A second notable feature of graphite is that it is compensated (electron and hole densities equal) and the theoretical quantum limit (QL) results of Kubo et al., [4] and of Adams and Holstein, [5] cannot be applied directly.

II. THEORY

McClure[6] has chosen a simple model which closely approximates graphite and assumes that scattering is by randomly placed, screened ionized impurities, where the screening is magnetic field dependent. The results of this theory give

$$\sigma_{xx} = K \frac{\pi}{16} (\Delta Z)^2 ec (n_s + p_s) B^{-1} \tag{1}$$

$$\sigma_{xy} = (p_s - n_s)\, ec\, B^{-1} \tag{2}$$

for the conductivity σ_{xx}, and Hall conductivity σ_{xy}, where two types of scatterers are assumed: ionized acceptors with density p_s, and ionized donors of density n_s. In (1) and (2) ΔZ is the valence difference from pure graphite. B is magnetic field and K is a constant equal to one in Ref. 6.

Refinements of this theory were made by Barnes[7] who showed that the coefficient in front of B^{-1} in (1) depended on the type of potential assumed, but that σ_{xx} was still proportional to B^{-1}.

Recently, Sugihara[8] has calculated σ_{xy} using details of the band structure of graphite for fields above 7 tesla, and finds deviation from the classical dependence on B^{-1}, as given in Eq. (2). This deviation was observed experimentally over a wide magnetic field range above 7 T, and is explained by Sugihara as due to the presence of neutral scattering centers.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A magnetic field was applied along the c-axis of several pressure-annealed pyrolytic graphite samples,[9] as well as in a natural single crystal. The magnetoresistivities, ρ_{xx}, and Hall resistivities, ρ_{yx}, were measured as functions of magnetic field and σ_{xx} and σ_{xy}, calculated from:

$$\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{yx}^2} \tag{3}$$

$$\sigma_{xy} = \frac{\rho_{yx}}{\rho_{xx}^2 + \rho_{yx}^2} \tag{4}$$

which are valid for the field along the c-axis. Temperatures were limited to 4.2 K and 1.5 K, and dc methods were used. Leads were attached with either conductive epoxy or copper plating and results were found to be independent of method.

Samples of pyrolytic graphite[10] were designated by PG followed by a number. PG9I was a neutron irradiated sample. Only one single crystal designated SC-1 was studied. In Table I the resistivities at 300 K and at 4.2 K are given, together with their ratios. These ratios are indicative of the purity/crystallinity of the samples. Samples PG9 and SC-1 have the highest ratios reported for any pyrolytic or single crystal respectively. At 4.2 K the average conductivity mobility for PG9 is $8 m^2/V \cdot s$, the highest reported for any pyrolytic material.

In Fig. 1, selected results of ρ_{xx} vs. B are given.[11] Of interest are the field dependencies above 7 tesla and the magnitude of ρ_{xx} at high field compared with the value in zero field. From results of ρ_{xx} and ρ_{yx} measurements, plots of σ_{xx} and σ_{xy} vs. B on log-log scales were made for each sample to

determine the field dependencies for comparison with Eqs. (1) and (2). Results on all samples are summarized in Table I. It is found that σ_{xx} is approximately proportional to B^{-1} up to about 15 T in most samples, as predicted by McClure et al.[6, 7]

In Fig. 2, σ_{xx} is plotted vs. B^{-1} and from Eq. (1) the slope should be proportional to $p_s + n_s$, the density of scattering centers, and these are listed in Table I. Since Eq. (1) is not followed over all field ranges, only the slopes below 15 T are used. From our Hall coefficient results and Eq. (2) we have calculated $n_s - p_s$ and these numbers are listed in Table I. The values of n_s and of p_s for the various samples are found to be nearly equal as shown in Table I. Such a result is very surprising, since it is unlikely that several samples would each have equal numbers of donor and acceptor impurities. It is more likely that only one type exists. Since the theoretical coefficient multiplying B^{-1} in Eq. (1) depended on the scattering potential assumed by McClure and Spry[6] and by Barnes and McClure,[7] it seems reasonable to use our data to adjust the coefficient. We thus assume that one type of scattering center dominates, and that the density is given by the Hall effect results. This assumption gives reasonable values for the relaxation time using the equations developed in Ref. 6. If the value of K in Eq. (1) is increased to 50, the densities determined by Eqs. (1) and (2) will be nearly the same. This value of K is closer to that found by Barnes and McClure than found previously by McClure and Spry. Further differences between $n_s + p_s$ and $|n_s - p_s|$ are then explainable as being due to differing amounts of more than one scattering type.

Another major result is a direct comparison with a recent theory by Sugihara[8] of the deviation[11] of σ_{xy} from B^{-1} dependence for SC-1. The Sugihara calculation uses the high field wavefunctions and energy levels unique

to graphite. Our experimental results are explained by the Sugihara theory if a density of ~ $10^{24}/m^3$ of neutral impurity centers is assumed.

Finally we would like to mention two experimental results which are unusual and as yet unexplained. The deviation from B^{-1} dependence of σ_{xx} above 15T (lower in PG3 and SC-1) has not been theoretically explained. A second unusual result is a decrease in the magnetoresistivity with decreasing temperature. Both of these results will be discussed more completely elsewhere.

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TABLE I. - QUANTITIES OBTAINED FROM EXPERIMENT FOR SEVERAL PYROLYTIC GRAPHITE SAMPLES, THE SINGLE CRYSTAL OF REFERENCE 6, AND A NATURAL SINGLE CRYSTAL ALL AT 4.2° K. (SYMBOLS ARE DEFINED IN TEXT.)

Sample	ρ_{xx} (300K) B = 0	ρ_{xx} (4.2K) B = 0	$\frac{\rho_{xx}(300K)}{\rho_{xx}(4.2K)}$ B = 0	k in $\sigma_{xx} \propto B^k$ 10 to 15 T	$n_s + p_s$ (σ_{xx} data 10 to 15 T)	$\lvert n_s - p_s \rvert$ (σ_{xx} data at 10 T)	n_s	p_s
PG3	0.5 $\mu\Omega$m	0.31 $\mu\Omega$m	1.6	S	1.3×10^{24} m^{-3}	0.02×10^{24} m^{-3}	0.64×10^{24} m^{-3}	0.66×10^{24} m^{-3}
PG4	0.51	0.06	8.5	-1.0^+	0.9	0.01	0.46	0.45
PG5	0.47	0.05	9.1	-1.1^+	1.2	0.04	0.62	0.58
PG7	0.53	0.11	5.0	-1.1^+	1.9	0.09	1.0	0.91
PG9	0.52	0.04	12.3	-1.1^+	1.1	0.005	0.54	0.55
PG9I	0.65	0.48	1.3	-0.5	1.8	--	--	--
Ref. 6	--	0.03	--	-1.0	0.7	0.01	0.36	0.35
SC-1	0.37	0.008	46	S	0.6	0.01	0.32	0.31

S Saturates to constant value.

+ Deviates above 15 T.

-- Not measured.

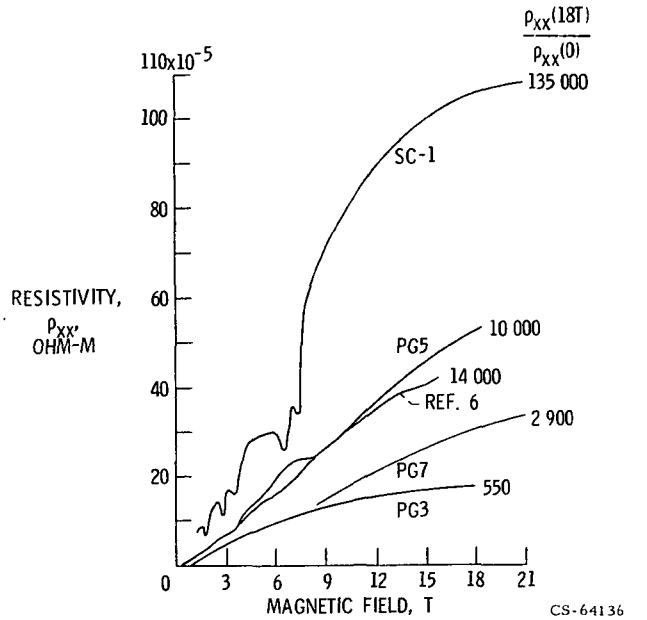

Figure 1. - Magnetoresistance, ρ_{xx} vs. magnetic field, for a selected set of pyrolytic and single crystal samples at 4.2 K. Numbers at right of curves indicate ratio of resistance at 18 T to the value at zero field.

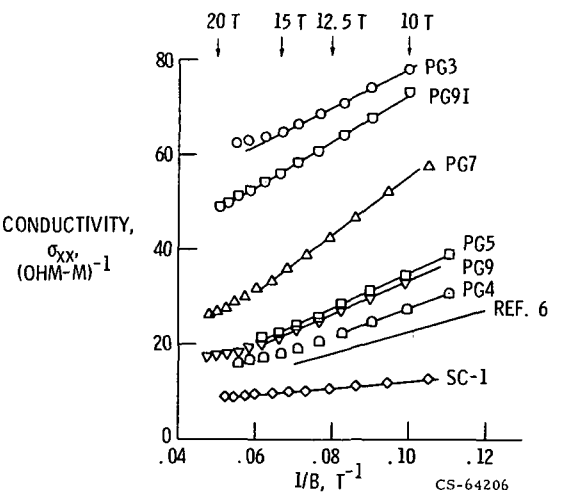

Figure 2. - Conductivities, σ_{xx} vs. magnetic field at 4.2 K for several pyrolytic samples and one single crystal. McClure and Spry's data are shown for comparison.